References

Plasma-Immersion Ion Implantation

Joseph V. Mantese, Ian G. Brown, Nathan W. Cheung, and George A. Collins

Introduction

Plasma-immersion ion implantation (PIII) is an emerging technology for the surface engineering of semiconductors, metals, and dielectrics.[1,2] It is inherently a batch-processable technique that lends itself to the implantation of large numbers of parts simultaneously. It thus offers the possibility of introducing ion implantation into manufacturing processes that have not traditionally been feasible using conventional implantation.

In PIII the part to be treated is placed in a vacuum chamber in which is generated a plasma containing the ions of the species to be implanted. The plasma-based implantation system does not use the extraction and acceleration methods of conventional mass-analyzing implanters. Instead the sample is (usually) repetitively pulsed at high negative voltages (in the 2–300 kV range) to implant the surface with a flux of energetic plasma ions as shown in Figure 1. When the negative bias is applied to a conducting object immersed in a plasma, electrons are repelled from the surrounding region toward the walls of the vacuum chamber, which is usually held at ground potential. Almost all the applied voltage difference occurs across this region, which is generally known as a sheath or cathode fall region. Ions are accelerated across the sheath, producing an ion flux to the entire exposed surface of the workpiece. Because the plasma surrounds the sample and because the ions are accelerated normal to the sample surfaces, implantation occurs over all surfaces, thereby eliminating the need for elaborate target manipulation or masking systems commonly required for beam line implanters. Ions implanted in the workpiece must be replaced by an incoming flow of ions at the sheath boundary, or the sheath will continue to expand into the surrounding plasma.

Plasma densities are kept relatively low, usually between 10^8 and 10^{11} ions per cm^3. Ions must be replenished near the workpiece by either diffusion or ionization since the workpiece (in effect) behaves like an ion pump. Gaseous discharges with thermionic, radio-frequency, or microwave ionization sources have been successfully used.

Surface-enhanced materials are obtained through PIII by producing chemical and microstructural changes that lead to altered electrical properties (e.g., semiconductor applications), and low-friction and superhard surfaces that are wear- and corrosion-resistant. When PIII is limited to gaseous implant species, these unique surface properties are obtained primarily through the formation of nitrides, oxides, and carbides. When applied to semiconductor applications PIII can be used to form amorphous and electrically doped layers. Plasma-immersion ion implantation can also be combined with plasma-deposition techniques to produce coatings such as diamondlike carbon (DLC) having enhanced properties. This latter variation of PIII can be operated in a high ion-energy regime so as to do ion mixing and to form highly adherent films, and in an ion-beam-assisted-deposition (IBAD)-like ion-energy regime to produce good film morphology and structure.

Tribological Applications

A primary focus of PIII today is concentrated on the implantation of nitrogen into metals for tribological applications. The focus on nitrogen is not surprising since conventional ion-beam implantation has demonstrated improved wear resistance of metals implanted with nitrogen ions.[3] Despite the extensive literature pointing to its benefits, ion-beam implantation has not been accepted to any great extent in the metallurgical surface-treatment industry due not only to the shallowness of the treatment depth but also because of the perceived difficulty in treating three-dimensional objects with a beam of accelerated ions.

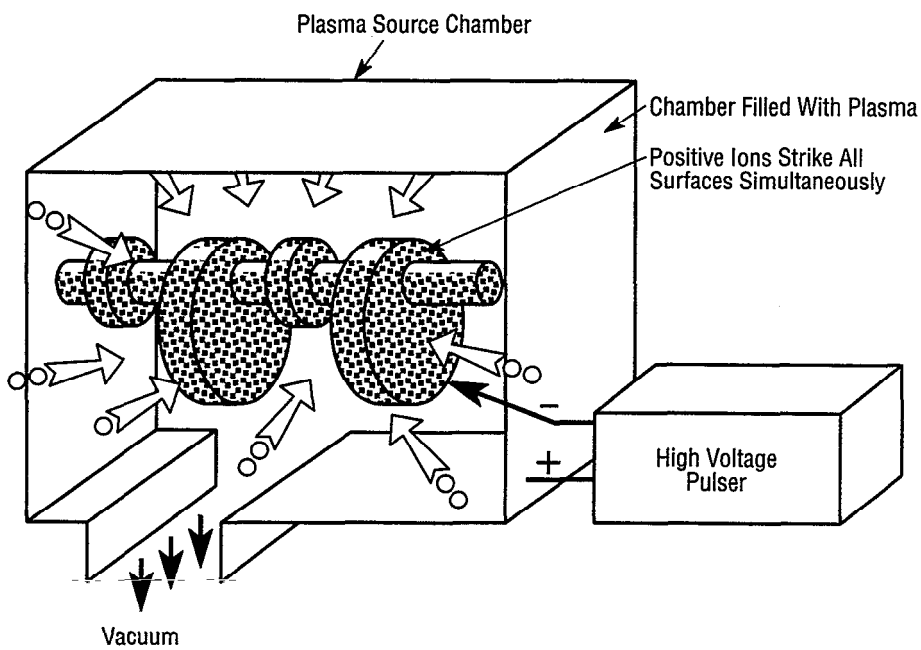

Figure 1. A plasma sheath surrounds the target in plasma-immersion ion implantation. Therefore ions bombard all surfaces simultaneously without beam aiming or target manipulation.

Implanting ions by PIII offers a solution to this latter problem.

A wide range of metals have been treated by PIII nitrogen implantation, yielding results as least as good as those obtained by conventional implantation. Examples of such materials include the following: Ti-6A1-4V,[4] Monel K-500,[5] AISI-S1 tool steel,[6,7] mild steel,[8] austenitic stainless steel,[9] aluminum[10], and hard chromium plate.[11] The implanted concentration profiles match well with those predicted by theory and despite the shallowness of the implantation depth (typically 50–100 nm at 50 keV), significant improvements in wear resistance have been obtained.

For example, almost no increase in microhardness could be detected after PIII-treatment of AISI S1 tool steel[7] but significant increases in wear resistance (from pin-on-disk wear testing) were obtained even at the highest load of 20 N. The implantation was carried out with 45 keV N_2^+ ions to a dose of 1×10^{18} atoms/cm^2.

Industrial applications of PIII have yielded some encouraging results.[12] These include the following: an 80% reduction in volumetric loss in AISI-M2 pierce punches used to produce holes in mild steel plate, a 65% improvement in service life of AISI-A2 tool-steel score dies used for manufacturing aluminum soft-drink cans, a 300% increase in lifetime of tooling used to manufacture high-strength structural bolts, and a 150% improvement in wear life of cobalt-cemented tungsten carbide drill bits used in printed circuit-board fabrication.[13]

In materials where the implanted species can diffuse, PIII at elevated temperatures can produce a substantial diffusion zone supporting the implanted layer, leading to major increases in hardness and load-bearing capacity.[14] In addition, extra nitrogen can be absorbed directly into the surface of the workpiece due to the chemical activity of the nitrogen plasma arising from a significant population of excited species, particularly atomic nitrogen and the metastable states of the nitrogen molecule and molecular nitrogen ions.

Early trials with both mild steel and austenitic stainless steel[8] showed diffusion of nitrogen well beyond the implantation range at temperatures above 250°C. Subsequent investigations of tool steels such as AISI-H13[15,16] at temperatures up to 500°C resulted in large increases in surface hardness due to the formation of a nitrogen-strengthened diffusion zone underlying the implanted layer. As the dose and temperature in-

Figure 2. Cross-sectional scanning-electron-microscope pictures of stained trench samples implanted at two bias conditions. The aspect ratio of the trenches is approximately 12.

creased, so did the extent and depth of hardening become greater.

Studies with a range of steels[7,14,17] have shown the important role of alloying elements in determining the depth of diffusion. In general the case thickness decreases in steels with a high proportion of nitride-forming alloying elements. For example, after treatment at 400°C for three hours, the case thickness in a low-alloy steel such as 17CrNiMo6 will be 80–100 μm but only 5 μm in AISI-316 stainless steel.

In some steels, extensive precipitation of γ'-Fe_4N and ε-Fe_2N_{1-x} occurs. These nitrides can influence the tribological performance of the treated surface.[7] In other materials, there is less nitride precipitation, and improvement in surface properties comes from nitrogen in solid solution. In AISI 316 stainless steel, a supersaturated "expanded-austenite" phase is produced[17] that has improved wear and corrosion resistance.[9] Pin-on-disk wear testing indicates that the wear rate is reduced by over two orders of magnitude even at the highest load.

Semiconductor Applications

The primary feature of PIII that makes it attractive for semiconductor processing is that a high-implantation dose rate may be achieved in a time independent of the implant area. Since the substrates are usually planar (e.g., Si wafers or glass panels), the design and operation of a semiconductor-based PIII system is greatly simplified, compatible with the cluster-tool concept for single-wafer processing. Such a system is expected to give lower production costs as compared to conventional beamline implanters.

Plasma doping in the low-energy regime is attractive for large-diameter Si wafer processing and for thin-film transistors (TFTs) used in flat-panel displays. These doping applications require a high dose rate but noncritical as-implanted depth profiles. For example, the final junction depth of sub-100 nm p^+/n junctions depends more on the post-annealing thermal cycle than the as-implanted depth profile.[18,19] Sub-100 nm p^+/n junctions fabricated by PIII usually show a diode ideality factor around 1.05 and have a bulk leakage-current density of approximately 2 nA/cm^2.[18–21] The first p-channel-metal-oxide-semiconductor processing integration using PIII was shown by Pico et al.[22] where PIII of BF was used to dope the p^+ source/drain and also the p^+ polysilicon gate. Recent work by Felch et al.[23] and Mizuno et al.[24] have demonstrated 0.15–0.25 μm metal-oxide-semiconductor field-effect transistors (MOSFET's).

Doping of polysilicon or silicides and hydrogenation of polysilicon thin-film transistors also depend on the dose rather than on the as-implanted profile. With the polysilicon TFT capped by 700 nm of SiO_2, PIII of hydrogen at 350°C with a bias of −6 kV has shown a significant reduction of process time to passivate the midgap grain boundary defects when compared to parallel-plate reactors with low radio-frequency bias.[25] This enhancement is explained by the high concentration dependence of diffusion with a large hydrogen incorporation in the plasma.

When PIII is operated at higher gas pressures (several mTorr), the slight beam divergence due to ion-neutral collisions can enhance microscopic conformal doping of nonplanar device structures (i.e., sidewalls of trenches). Sidewall doping is accomplished by both direct implantation and reflected implantation. Conformal doping of trenches using plasma doping was first demonstrated by Mizuno.[26] That work showed that the angular divergence of the ions in the PIII implant was large enough to conformally dope a trench with an opening of 0.45 μm and a depth of 2.8 μm. Higher aspect-ratio trenches have been doped by PIII, including the example shown in Figure 2 where the aspect ratio was 12 and the opening was 1 μm.[27] In this figure, the junction depth was delineated by selective etching in a 30:1 HNO_3:HF solution. The figure shows a uniform electrical-junction depth along the sidewalls of the trench with no evidence of beam shadowing.

Other applications related to semiconductor processing are selective electroless plating of copper interconnects in SiO_2 trenches by Pd and Pd/Si seeding,[28,29] and backside gettering of metallic impurities in Si.[30] In the low-energy regime (~1 kV), dose incorporation in the substrate is limited by surface sputtering. In the high-energy regime, the dose rate is so high that reproducible control for low-dose implants becomes difficult.

Enhanced Processes

When a gaseous plasma impinges on a solid surface, the ions recombine at the surface and generally an equilibrium is reached in which neutral gas atoms recycle to the plasma at the same rate as ions strike the surface. However, when the plasma in which the object is immersed is derived from a metal or metal-organic species (a complex molecular plasma with a metal constituent), the plasma condenses and remains on the substrate as a film. Because of this surface retention, the PIII process in such a plasma is quite different from in a gaseous plasma, and qualitatively new and different consequences follow.[31–34]

With a metal plasma, ions accelerated by the high-voltage-bias pulse impact previously deposited surface metal atoms to produce recoil implantation. Thus the depth profile of this process is quite different from the usual gaussian-like shape and extends from the surface down to the maximum range. By varying the ratio of pulse-on time (during which implantation occurs) to pulse-off time (during which deposition occurs) the shape of the profile can be tailored. An early-time high-energy ion implant can be used to automatically mix the film into the substrate followed by a lower but optimized ion-energy implant during the bulk of the film growth to add an "ion-assisted" or IBAD-like process. In this way, films can be made that have strong adhesion, high density (void-free), good structure (not columnar), and good morphology (close to atomically smooth).

Alternatively by operating in the appropriate parameter regime (primarily by adjusting the pulse-bias duty cycle) and taking advantage of surface sputtering due to the energetic ion bombardment, one can produce modified surfaces that are pure implants with no surface film.[35] In a closely related plasma-immersion technique,[32] the high voltage bias is maintained at constant potential and the metal-plasma gun is repetitively pulsed, resulting in a pure implantation profile.

Metal plasmas can be efficiently generated from solid metals by a vacuum-arc discharge, also called a cathodic arc in some regimes. This technique has been developed and exploited by many workers.[36–38] Along with the metal plasma generated in a cathodic arc, a flux of cathode debris (called macroparticles) of size typically 0.1–10 microns is also produced. This contamination can be filtered out by a curved magnetic duct, which stops line-of-sight transmission of macroparticles while allowing the transmission of plasma.[39]

The process described is applicable to all kinds of condensable plasmas, including metal compounds and alloys, semiconductors, and carbon. More than one kind of metal species can be applied, either simultaneously or sequentially. Nonequilibrium alloys can be synthesized using cathodes made from pressed powders or by using multiple plasma guns. By adding a gas (or gaseous

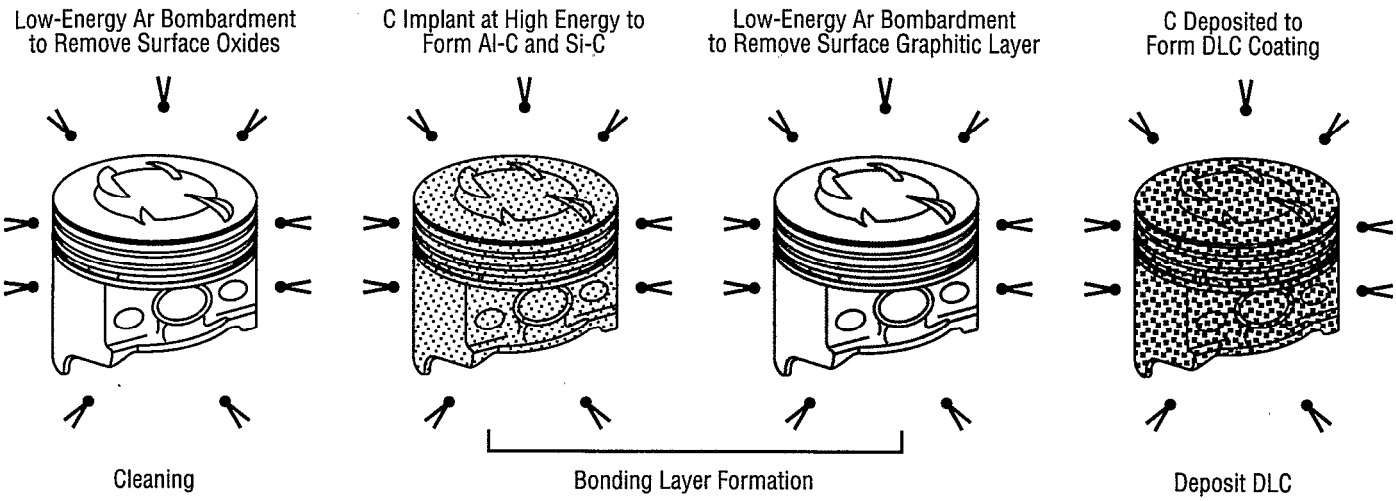

Figure 3. Schematic diagram showing the sequence for producing highly adherent diamondlike-carbon films on aluminum 390 alloy using plasma-immersion ion implantation.

plasma) to the metal-plasma implantation-and-deposition process, one can produce atomically mixed metal oxides and nitrides[40] as well as high T_c superconducting thin films (precursor alloys),[41] and ceramics such as alumina and chromia.[42]

Hydrogen-free DLC films have also been made by this process.[43,44] The films are ion-stitched to the substrate and have hardness up to 60 GPa, adhesion >80 MPa, a density of 3.0 g/cm^3 (thus quite void-free), and sp^3 (diamond-bonding) fraction up to 85%. By periodically varying the carbon ion energy, multilayer structures of "hard" and "soft" DLC can be made.[45]

Pulsed-bias deposited coatings of DLC on metal substrates from gaseous sources often lack sufficient adhesion for tribological applications. In particular, the adhesion of DLC (produced from either a methane- or acetylene-derived plasma) on aluminum 390 alloy showed that the coating possessed minimal adhesive strength (below the sensitivity of the testing device) with failure occurring at the DLC/Al-390 interface. However moderate-energy PIII carbon implantation can be used in conjunction with DLC deposition to dramatically increase adhesion using the methodology described in Figure 3 and shown for piston applications in the photograph on the cover of this issue of *MRS Bulletin*.

Scalability and Cost

The true potential for large-scale commercial applications of PIII for manufacturing remains largely unknown. However there have been a number of experiments[13,46] and modeling studies[47,48] suggesting that PIII can be scaled without limit. This latter work however assumed that the plasma distribution remained uniform over the entire array of parts and that the switching electronics could supply sufficient current to account not only for the ion current but for the electron current as well. For large-volume PIII systems where a large number of secondary electrons are created (such as with aluminum), these issues become critical in achieving uniform implants over the entire array of target components. However magnetic[49] and electrostatic confinement of secondaries is believed to be a possible method of suppressing the large electron current from such materials.

Conservative cost estimates of PIII for high-volume manufacturing are of the order of ~$0.01 cm^{-2},[50] and indicate that this process is a competitive technology when compared to similar manufacturing processes such as evaporation and sputtering. The greatest cost arises from the amortization of capital investment and rent.

Plasma-immersion ion implantation builds upon the tremendous background research and knowledge base of beam-line ion implantation. However PIII advances ion implantation into manufacturing arenas that have traditionally been reluctant to adopt advanced processing technologies by virtue of its ability to implant complex three-dimensional shapes with adequate uniformity, process multiple components simultaneously, and eliminate the need for complicated target manipulation or masking. There are however limitations to the applicability of PIII in that beam-line implantation will always be essential where mass-resolved ions are required. When combined with other existing surface-modification processes such as plasma nitriding, ion-assisted deposition, or ion mixing, PIII offers exciting possibilities for new methods of materials processing and materials synthesis.

References

1. J.R. Conrad, J.L. Radtke, R.A. Dodd, F.J. Worzala, and N.C. Tran, *J. Appl. Phys.* **62** (1987) p. 4591.
2. J. Tendys, I.J. Donnelly, M.J. Kenny, and J.T.A. Pollock, *Appl. Phys. Lett* **53** (1988) p. 2143.
3. W.C. Oliver, R. Hutchings, and J.B. Pethica, *Metall. Trans. A* **15** (1984) p. 2221.
4. X.Qiu, J.R. Conrad, R.A. Dodd, and F.Y. Worzala, *ibid.* **21** (1990) p. 1663.
5. M.S.P. Madapura, R.A. Dodd, J.R. Conrad, D. Plantz, and F.J. Worzala, *J. Vac. Sci. Technol. A* **8** (1990) p. 2169.
6. A.M. Redsten, K. Sridharan, and F.J. Worzala, *J. Mater. Process. Technol.* **30** (1992) p. 253.
7. M. Samandi, A. Pauza, G. Hatziandoniou, H. Yasbandha, R. Hutchings, G.A. Collins, and J. Tendys, *Surf. Coat. Technol.* **54/55** (1992) p. 447.
8. G.A. Collins, R. Hutchings, and J. Tendys, *Mater. Sci. Eng. A* **139** (1991) p. 171.
9. M. Samandi, B.A. Shedden, D.I. Smith, G.A. Collins, R. Hutchings, and J. Tendys, *Surf. Coat. Technol.* **59** (1993) p. 261.
10. K.C. Walter, *J. Vac. Sci. Technol. B* **12** (1994) p. 945.
11. K.C. Walter, J.T. Scheuer, P.C. McIntyre, P. Kodai, N. Yu, and M. Nastasi, *Surf. Coat. Technol.* **84** (1–2) (1996).
12. S.M. Malik, K. Sridharan, R.P. Fetherston, A. Chen, and J.R. Conrad, *J. Vac. Sci. Technol. B*

12 (1994) p. 843.
13. J.N. Matossian, J.J. Vajo, J.A. Wysocki, and M.E. Bellon, *Surf. Coat. Technol.* **62** (1993) p. 595.
14. G.A. Collins, R. Hutchings, and J. Tendys, *ibid.* **59** (1993) p. 267.
15. R. Hutchings, G.A. Collins, and J. Tendys, *ibid.* **51** (1992) p. 489.
16. R. Hutchings, M.I. Kenny, D.R. Miller, and W.Y. Yeung, in *Proc. 1st Aust. Int. Conf. on Surface Engineering: Practice and Prospects* (Adelaide, March 1991).
17. G.A. Collins, R. Hutchings, K.T. Short, J. Tendys, X. Li, and M. Samandi, *Surf. Coat. Technol.* **74/75** (1995) p. 417.
18. E.C. Jones and N.W. Cheung, *IEEE Electron. Dev. Lett.* **14** (1993) p. 444.
19. T. Sheng, S.B. Felch, and C.B. Cooper, *J. Vac. Sci. Technol. B* **12** (1994) p. 969.
20. X.Y. Qian, N.W. Cheung. M.A. Lieberman, S.B. Felch, R. Brennan, and M.I. Current, *Appl. Phys. Lett.* **59** (1991) p. 348.
21. B. Mizuno, H. Nakaoka, M. Takase, A. Hori, F. Nakayama, and M. Ogura, *Ext. Abstr. of 1995 Int. Conf. on Solid State Dev. Mater.* (Osaka, Japan, August 1995) p. 1041.
22. C.A. Pico, M.A. Lieberman, and N.W. Cheung, *J. Electron. Materials* **21** (1992) p. 75.
23. S.B. Felch, to be published.
24. B. Mizuno, I. Nakayama, M. Takase, H. Nakaoka, and M. Kubota, *Surf. Coat. Technol.* **84** (1–2) (1996).
25. J.D. Bernstein, S. Qin, C. Chan, and T-J. King, *IEEE Electron. Dev. Lett.* **16** (1995) p. 421.
26. B. Mizuno, I. Nakayama, N. Aoi, M. Kubota, and T. Komeda, *Appl. Phys. Lett.* **53** (1989) p. 2059.
27. C. Yu and N.W. Cheung, *IEEE Electron. Dev. Lett.* **15** (1994) p. 196.
28. M. Kiang. M.A. Lieberman, N.W. Cheung, and X.Y. Qian, *Appl. Phys Lett.* **60** (1992) p. 2767.
29. X.Y. Qian, M.H. Kiang, N.W. Cheung, I. Brown, X. Godehot, J.E. Galvin, R.A. MacGill, and K.M. Yu, *Nuclear Instrum. Methods B* **55** (1991) p. 893.
30. X.Y. Qian, H. Wong, D. Carl, M.A. Lieberman, and N.W. Cheung, *ECS Proc.* **90-13** (1990) p. 174.
31. I.G. Brown, X. Godechot, and K.M. Yu, *Appl. Phys. Lett.* **58** (1991) p. 1392.
32. T. Sroda, S. Meassick, and C. Chan, *ibid.* **60** (1992) p. 1076.
33. I.G. Brown, A. Anders, S. Anders, M.R. Dickinson, I.C. Ivanov, M.A. MacGill, X. Yao, and K.M. Yu, *Nucl. Instrum. Methods B* **80/81** (1993) p. 1281.
34. A. Anders, S. Anders, I.G. Brown, M.R. Dickinson, and R.A. MacGill, *J. Vac. Sci. Tech. B* **12** (1994) p. 815.
35. A. Anders, S. Anders, I.G. Brown, and K.M. Yu, *9th Int. Conf. Ion Beam Mod. Mat.* (Canberra, Australia, February 5–10, 1995).
36. J.M. Lafferty, ed., *Vacuum Arcs—Theory and Application* (John Wiley & Sons, New York, 1980).
37. R.L. Boxman, P. Martin, and D. Sanders, eds., *Vacuum Arc Science and Technology* (Noyes, New York, 1995).
38. R.J. Adler and S.T. Picraux, *Nucl. Instrum. Methods B* **6** (1985) p. 123.
39. A. Anders, S. Anders, and I.G. Brown, *Plasma Sources Sci. Technol.* **4** (1995) p. 1.
40. R.A. MacGill, S. Anders, A. Anders, R.A. Castro, M.R. Dickinson, K.M. Yu, and I.G. Brown, *Surf. Coat. Technol.* **78** (1996) p. 168.
41. M.S. Chae, M.B. Maple, M.T. Simnad, S. Anders, A. Anders, and I.G. Brown, *IEEE Trans. Appl. Supercon.* **5** (1995) p. 2011.
42. P.Y. Hou, K.B. Alexander, Z. Wang, and I.G. Brown, presented at TMS Annual Meeting, Symposium on High Temperature Coatings, Anaheim, CA, Feb. 4–8, 1996.
43. S. Anders, A. Anders, C.S. Bhatia, S. Raoux, D. Schneider, J.W. Ager III, and I.G. Brown, in *Proc. 3rd Int. Conf. Applications Diamond Films Related Mater.*, Gaithersburg, MD, Aug. 21–24, 1995 (NIST special pub. 885, Washington, DC, 1995) p. 809.
44. S. Anders, A. Anders, I.G. Brown, B. Wei, K. Komvopoulos, J.W. Ager III, and K.M. Yu, *Surf. Coat. Technol.* **68/69** (1994) p. 383.
45. S. Anders, G.M. Pharr, T.Y. Tsui, D.L. Callahan, and C.S. Bhatia (unpublished manuscript).
46. B.P. Wood, I. Henins, R.J. Gribble, W.A. Reass, R.J. Faehl, M.A. Nastasi, and D.J. Rej, *J. Vac. Sci. Technol. B* **12** (1994) p. 870.
47. R. Faehl, B. De Volder, and B. Wood, *ibid.* **B12** (1994) p. 884.
48. M. Hong and G.A. Emmert, *ibid.* p. 889.
49. D.J. Rej, B.P. Wood, R.J. Gaehl, and H.H. Fleischmann, *ibid.* p. 861.
50. D.J. Rej and R.B. Alexander, *ibid.* p. 2380. □